

# PATENT SPECIFICATION

(11) 1250 516

1250 516

NO DRAWINGS

- (21) Application No. 22086/69
- (22) Filed 30 April 1969
- (23) Complete Specification filed 27 April 1970
- (45) Complete Specification published 20 Oct. 1971
- (51) International Classification C 08 b 11/20 19/10
- (52) Index at acceptance

C3A 1 4C1  
C3U 10E 12B2G 12B2J 2C2 3B 4E

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## (54) IMPROVEMENTS IN AND RELATING TO DEFLOCCULANT AND DISPERSING AGENTS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of improved deflocculant and dispersing agents. Polysaccharide deflocculants and dispersing agents, including certain cellulose ethers and alginates, are used extensively in industrial processes. The literature suggests that the lower the viscosity of the polysaccharide, i.e. the viscosity exhibited by solutions of the polysaccharide, the higher is its efficiency as a deflocculant and dispersing agent.

We have discovered that lowering the viscosity of certain polysaccharide derivatives below a critical value is of particular advantage but that it is extremely difficult to obtain such low viscosity materials in a readily marketable granular or powder form when the reduction in viscosity is achieved by conventional methods.

In the case of cellulose ethers, for instance, several methods are known for reducing their viscosities and obtaining the product as a powder or granules. In one method the viscosity of the cellulose ether is controlled by controlling the degree of degradation of the cellulose from which the ether is subsequently prepared. This method of viscosity control has the disadvantage that the cellulose degradation effected is not uniform. Consequently the low viscosity cellulose ether contains portions which are excessively soluble in, and are consequently difficult to isolate from, the strongly alkaline liquors in which they are prepared.

More efficient methods of reducing the viscosities of cellulose ethers involve oxidative degradation of the ethers by oxidising agents such as hydrogen peroxide, sodium hypochlorite and the like. The problem of isolating the low viscosity product is circumvented in these

methods by taking steps to avoid carrying out the oxidative degradation with the cellulose ether in solution so that, as in the previously described method, the product is obtained in a solid marketable form. One of said methods comprises a slurry treatment in which hot water-insoluble cellulose ethers such as methyl cellulose, methyl ethyl cellulose and hydroxymethyl ethyl cellulose are treated in aqueous suspension with hydrogen peroxide. In the case of hot water-soluble cellulose ethers, such as sodium carboxymethyl cellulose and hydroxyethyl cellulose, an alcohol is included in the reaction mixture to prevent the cellulose ether from going into solution. In yet another method, which does not require the presence of an alcohol, the oxidative degradation is effected with a limited amount of water present, sufficient to moisten the ether but not to dissolve it. All these methods have in common the production of a low viscosity cellulose ether which is in solid form such as fibres, granules or powder.

According to the present invention a deflocculant and dispersing agent is prepared by oxidatively degrading an alkali metal, amine or ammonium salt of a higher viscosity water-soluble anionic polysaccharide in aqueous solution to reduce the viscosity of the polysaccharide derivative to a value in the range of 10 to 50 centipoises at 15% concentration in water when measured at 20°C.

The desired viscosity is preferably obtained by controlling the duration and temperature of the degradation.

The end product of the degradation process of the invention is an aqueous solution of the low viscosity polysaccharide but the dispersant and deflocculation action of polysaccharide solutions having such viscosities is so efficient that there is no need to attempt to isolate the polysaccharide from solution.

The anionic groupings of the polysaccharide are preferably carboxyl and sulphate.

As an oxidising agent for use in the process of the invention, hydrogen peroxide is pre-

ferred since its by-product in the oxidation process is water, although it is also possible to use other oxidising agents such as sodium hypochlorite. Examples of salts of anionic polysaccharides suitable for employment in the process of the invention include sodium carboxymethyl cellulose, potassium alginate and ammonium alginate. Sodium alginate and sodium cellulose sulphate may also be employed.

The process of the invention may be carried out by adding aqueous hydrogen peroxide to an aqueous solution or suspension of the polysaccharide derivative of 14 to 16% concentration. In a modified technique the hydrogen peroxide solution and the polysaccharide derivative may be added separately in a continuous manner or in recurring aliquots to a quantity of water and the viscosity of the resultant solution is checked at regular intervals until a value is obtained in a range corresponding to 10 to 50 centipoises at 15% concentration and 20°C. It is also possible by these techniques to prepare solutions of the oxidised polysaccharide derivative above 15% concentration which can be advantageously employed as deflocculants and dispersing agents in chemical formulations.

The process of the invention may be carried out at a temperature in the range 20°C. to 100°C. and when hydrogen peroxide is employed as the oxidising agent the preferred temperature is 40°C to 80°C. To obtain reaction in a reasonable time, and from the point of view of economy, it is preferred to use the oxidising agent in a quantity corresponding to 0.7 to 1.5 parts by weight available oxygen per 100 parts by weight of polysaccharide derivative.

The present invention is also a deflocculant and dispersing agent comprising an aqueous solution of an alkali metal, amine or ammonium salt of a water-soluble anionic polysaccharide having a viscosity in the range 10 to 50 centipoises at 15% concentration when measured at 20°C.

The present invention is also a formulation including as a dispersant or deflocculating agent an aqueous solution of an alkali metal, amine or ammonium salt of a water-soluble anionic polysaccharide having a viscosity of 10 to 50 centipoises at 15% concentration when measured at 20°C.

Preferably the formulation is a china clay dispersion containing the dispersant at a dosage level of 0.2 to 0.4% on a dry solids basis on the weight of clay.

As mentioned above, dispersing agents are widely used in industrial processes. For example, a physical mixture of china clay with its own weight of water is a friable solid mass which requires a considerable amount of mechanical treatment to achieve even a putty-like consistency. However, on the addition of small amounts of a dispersing agent such as sodium

hexametaphosphate, the mixture is transformed to smooth, thin, creamy consistency. This has obvious usefulness, for example, in the use of china clay to coat paper and in the dispersion of pigments for paint manufacture.

The aforementioned dispersant, sodium hexametaphosphate, is widely used but suffers from a number of disadvantages. Thus, it is hydrolysed at elevated temperatures which results in a loss of dispersant efficiency in processes such as paper coating where starches are employed as the binder and pasting of the starches at elevated temperatures is required. Again, since sodium hexametaphosphate sequesters calcium ions, larger quantities are required when hard water is used. Also, it has been observed that its dispersing efficiency is greatly reduced by the presence of soluble inorganic salts in general. This ion sensitivity is also a disadvantage of other known dispersing agents such as sodium polyacrylate.

The low viscosity polysaccharide derivatives prepared by the process of the invention are particularly useful in the dispersion of paper grades of china clay and also for the dispersion of titanium dioxide, calcium carbonate and other pigments employed in paper coating and emulsion paints. They are also useful in the dispersion of insecticides and fungicides and for minimising sludge deposition in various industrial scrubbing and cleaning processes. They are dispersing agents of extremely high efficiency, with excellent heat stability, storage stability and ion tolerances, superior to the above mentioned known dispersants.

The invention is further illustrated by the following Examples, in which all parts and percentages are by weight.

#### EXAMPLE 1

60 parts of sodium carboxymethyl cellulose, with a degree of substitution of 0.7 carboxymethyl substituents per anhydroglucose unit and a viscosity of 40 centipoises in 3% aqueous solution measured at 20°C using a U-tube viscometer of appropriate size, type BS/U to BS 188 1957, were dissolved in 335.5 parts water and 4.5 parts of 100 volume hydrogen peroxide added. The solution was heated for 90 minutes at 80°C in a hot water bath while stirring, and excess hydrogen peroxide was then removed by boiling gently with constant stirring till a negative result was obtained on testing for the presence of peroxide. The solution was cooled and made up to 400 parts to replace water lost through evaporation during heating at 80°C and subsequent boiling and so obtain a 15% by weight solution of sodium carboxymethyl cellulose. The viscosity of this solution, as measured using spindle 1, speed 20 on a Brookfield RV Viscometer, was 27 centipoises and the viscosity of a 60% solids china clay dispersion prepared using this solu-

tion as dispersant, 170 centipoises at a dosage level of 0.4% on a dry solids basis on the weight of clay.

#### EXAMPLE 2

5 The same procedure was used as for Example 1 but using 3 parts of 100 volume hydrogen peroxide to 60 parts of the same grade of sodium carboxymethyl cellulose and 337  
10 parts water and heating for 120 minutes at 80°C. The viscosity of the 15% by weight sodium carboxymethyl cellulose solution prepared was 38 centipoises and the viscosity of a 60% solids china clay dispersion prepared using this solution as dispersant, 180 centipoises at 0.4% dosage level on a dry solids  
15 basis on the weight of china clay.

#### EXAMPLE 3

The procedure was as for the previous Examples but using 6 parts of 100 volume hydrogen peroxide to 60 parts of the same grade of sodium carboxymethyl cellulose and 334  
20 parts water and heating for 60 minutes at 80°C. The viscosity of the 15% by weight sodium carboxymethyl cellulose solution prepared was 40 centipoises and the viscosity of a 60% solids china clay dispersion prepared using this solution as dispersant, at 0.4% dosage level on a dry solids basis on the weight of clay, 135 centipoises.

#### EXAMPLE 4

30 60 parts sodium carboxymethyl cellulose, with a degree of substitution of 0.7 carboxymethyl substituents per anhydro-glucose unit and a viscosity of 40 centipoises in a 1% aqueous solution at 20°C using a U-tube viscometer of appropriate size, type BS/U to BS 188 1957, were added to an aqueous solution of 4.5 parts of 100 volume hydrogen peroxide in 335.5 parts water, which had been  
40 preheated to 80°C before addition of the sodium carboxymethyl cellulose, with vigorous stirring to disperse the sodium carboxymethyl cellulose. The sodium carboxymethyl cellulose suspension in aqueous hydrogen peroxide was  
45 heated for 90 minutes at 80°C, with stirring when possible, boiled gently to remove excess peroxide and the viscosity of the solution, after making up to 15% by weight sodium carboxymethyl cellulose, measured as for the  
50 previous Examples. The viscosity of the 15% sodium carboxymethyl cellulose solution was 38 centipoises, and the viscosity of a 60% solids china clay dispersion prepared using this solution as dispersant at 0.4% dry solids dosage level on the weight of clay was 170  
55 centipoises.

#### EXAMPLE 5

60 As for Example 4, but the sodium carboxymethyl cellulose was added with vigorous stirring to cold aqueous hydrogen peroxide solution and the sodium carboxymethyl cellulose

suspension heated for 120 minutes at 80°C. The viscosity of the 15% by weight sodium carboxymethyl cellulose solution prepared was 25 centipoises and the viscosity of a 60% solids china clay dispersion 190 centipoises, the dispersion being prepared using the degraded solution a 0.4% dry solids dosage level on the weight of china clay.

#### EXAMPLE 6

70 In this Example 60 parts of ammonium alginate, such that a 1% aqueous solution at 20°C had a viscosity of 14 centipoises measured by a Brookfield Viscometer U.L. adaptor speed 30 r.p.m., were dispersed in an aqueous solution of 4.5 parts of 100 volume hydrogen peroxide in 335.5 parts of water and heated at 80°C to 85°C for 180 minutes, stirring when possible. Excess peroxide was  
80 boiled off and the resulting solution of low molecular weight ammonium alginate made up to 400 parts or 15% by weight of the ammonium alginate by the addition of water to replace water lost through evaporation during heating at 80°C to 85°C or subsequent  
85 boiling to remove excess peroxide. The viscosity of the 15% alginate solution was 12.5 centipoises and a 60% china clay dispersion prepared using the alginate solution as dispersant at 0.4% dry solids dosage level on the weight of clay was 52.5 centipoises.

#### EXAMPLE 7

Potassium alginate, such that a 1% aqueous solution at 20°C had a viscosity of 90 centipoises measured by a Brookfield Viscometer, spindle 1, speed 60 r.p.m., was prepared using the same procedure as for Example 6. The viscosity of the 15% alginate solution was 15.0 centipoises and of a 60% solids china clay dispersion prepared using the degraded potassium alginate solution as dispersant at 0.4% dry solids dosage level was 60 centipoises.

#### WHAT WE CLAIM IS:—

1. A method of manufacturing a deflocculant and dispersing agent comprising oxidatively degrading an alkali metal, amine or ammonium salt of a higher viscosity water-soluble anionic polysaccharide to reduce the viscosity of the polysaccharide derivative to a value in the range 10—50 centipoises when measured at 15% concentration in water at 20°C.

2. A method as claimed in Claim 1 wherein said viscosity is obtained by controlling the duration and temperature of the degradation.

3. A method as claimed in Claim 1 or Claim 2 wherein the oxidising agent used for the degradation is hydrogen peroxide or sodium hypochlorite.

4. A method as claimed in any one of Claims 1 to 3 wherein the salt of the anionic

polysaccharide is a salt of a cellulose ether or ester.

5. A method as claimed in any one of Claims 1 to 4 wherein the anionic grouping of the polysaccharide salt is carboxyl or sulphate.

6. A method as claimed in any one of Claims 1 to 3 wherein the salt of the anionic polysaccharide comprises sodium carboxymethyl cellulose, sodium cellulose sulphate, potassium alginate, sodium alginate or ammonium alginate.

7. A method as claimed in any one of Claims 1 to 6 wherein the oxidative degradation is effected by adding aqueous hydrogen peroxide to an aqueous solution or suspension of the polysaccharide salt of 14 to 16% concentration.

8. A method as claimed in any one of Claims 1 to 6 comprising adding hydrogen peroxide solution and the polysaccharide salt separately in a continuous manner or in recurring aliquots to a quantity of water and checking the viscosity of the resulting solution at regular intervals until the desired viscosity is obtained.

9. A method as claimed in any one of the preceding claims carried out at a temperature in the range 20°C to 100°C.

10. A method as claimed in Claim 9 carried out at a temperature in the range 40 to 80°C.

11. A method as claimed in any one of the preceding claims wherein the oxidising agent is used in a quantity corresponding to 0.7 to 1.5 parts by weight available oxygen per 100 parts by weight of the polysaccharide salt.

12. A method of manufacturing a deflocculant and dispersing agent as claimed in Claim 1 and substantially as hereinbefore described.

13. A deflocculant and dispersing agent

comprising an aqueous solution of an alkali metal, amine or ammonium salt of a water-soluble anionic polysaccharide having a viscosity in the range 10 to 50 centipoises at 15% concentration when measured at 20°C.

14. A deflocculant and dispersing agent as claimed in Claim 13 wherein the salt of the anionic polysaccharide comprises a salt of a cellulose ether or ester.

15. A deflocculant and dispersing agent as claimed in Claim 13 or Claim 14 wherein the anionic grouping of the polysaccharide salt comprises carboxyl or sulphate.

16. A deflocculant and dispersing agent as claimed in Claim 13 wherein the salt of the anionic polysaccharide comprises sodium carboxymethyl cellulose, sodium cellulose sulphate, potassium alginate, sodium alginate or ammonium alginate.

17. A deflocculant and dispersing agent prepared according to the method of any one of Claims 1 to 12.

18. A deflocculant and dispersing agent substantially as hereinbefore described with reference to the Examples.

19. A formulation comprising a dispersant or deflocculating agent as claimed in any one of Claims 13 to 18.

20. A china clay dispersion comprising a dispersing agent as claimed in any one of Claims 13 to 18.

21. A china clay dispersion as claimed in Claim 20 containing the dispersing agent at a dosage level of 0.2 to 0.4% on a dry solids basis on the weight of clay.

22. A paint comprising a dispersing agent as claimed in any one of Claims 13 to 18.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.